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Effect of annealing on the structural and optical properties of SILAR grown Cu_xS thin films

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Abstract : Thin films of copper sulphide (Cu_xS) with thickness up to 0.5 μm were deposited on glass substrates using simple successive ionic layer adsorption and reaction (SILAR) method. Copper (II) sulphate complexed with triethaneloamine (TEA) and thiourea were used as (cuprous ions) cation and (sulphide ions) anion precursors, respectively. The deposition was carried out at room temperature with optimized conditions. The as deposited samples were annealed in air at 100, 200, 300, 400 and 500°C for one hour These films were characterized by means of X-ray diffraction and optical absorption techniques.

Keywords : Annealed thin films, X-ray diffraction, optical absorption

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1 Introduction

Copper sulphide (Cu_xS) represents an interesting class of semiconducting material, which are attractive for large scale applications because of easy availability and low cost of the starting materials. Cu_xS as a material particularly in its thin film form has received attention since the discovery of the photovolatic effect in CdS – Cu_xS [1]. Detailed studies on the Cu_xS system in the context of photovolatic applications were reported [2, 3]. In the bulk form, Cu_xS is known to exit in five stable phases at the room temperature with orthorhombic (Cu_2S) on the 'copper deficient' side of the phase diagram of the Cu-S system. In the composition closer to the stoichiometric Cu_2S, the distinct room temperature phases are the orthorhombic chalcocite ($1.95 \leq x \leq 2.00$), djurleite ($1.93 \leq x \leq 1.96$) and digenite ($1.765 \leq x \leq 1.79$). In the intermediate composition, mixed phases such as chalcocite + djurleite and djurleite + digenite are commonly observed. It is interesting that these distinct compositions are not remarkable about crystalline structure but in the variation of electrical conductivity [4] and significant variation in optical band gap [5]. The stability of CdS – Cu_xS heterojunction solar cell involves the stability of short circuit current (I_{sc}). The I_{sc} is a function of x in Cu_xS, as x increases I_{sc} also increases and attains maximum value at $x = 2$ [2].

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Numerous techniques for producing copper sulphide thin films have been investigated. These include vacuum evaporation [6], activated reactive evaporation [7], reactive magnetron sputtering [8], spray pyrolysis [9], sulphurisation of copper foils and films [10] and slurry technique [11]. Chemical bath deposition of copper sulphide (Cu_xS) thin films from alkaline [12-14] and acidic [15] medium has been investigated.

Recent studies [16] have shown that chemically as deposited CuS thin films undergo compositional changes upon annealing in nitrogen for 1 h to $Cu_{1.8}S$ (300°C) and to $Cu_{1.96}S$ (400°C) from CuS. This transformation was accompanied by changes in electrical and optical properties.

In an earlier publication, we reported [17] the deposition of copper sulphide (Cu_xS) thin films using successive ionic layer adsorption and reaction (SILAR) method. The purpose of the present paper is to describe the preparation of copper sulphide thin films by SILAR method using complexant. In our earlier studies [17], copper sulphide (Cu_xS) thin films were deposited without any complexing agents. We have observed that as deposited films consist Cu_xS ($1.96 \leq x \leq 1.86$) and Cu_2S phases. In this paper triethaneloamine (TEA) is used as the complexing agent to form uniform and adherent Cu_xS thin films. Use of triethaneloamine (TEA) as a complexing agent gives *CuS* phase. Effect of air annealing on the structural and optical properties of SILAR grown Cu_xS thin films are reported.

2. Experimental details

2.1 Deposition :

In the present work, microslide glass slides (75 mm × 25 mm × 1 mm) were used as substrates. Prior to the deposition of the films, these substrates were cleaned using commercial detergent and double distilled water and dried with hot air. The cationic precursor was 0.2 M copper sulphate solution complexed with triethaneloamine (TEA) (0.1 M). The pH was adjusted to about 10 by adding liquid ammonia. The source of sulphide ions was 0.1 M thiourea solution (pH ~ 6). Prepared solutions were taken into beakers of capacity 50 ml each. For rinsing purpose, ample quantity of double distilled water (resistivity ~ 18 MΩ cm) was used. After 5 deposition cycles, water was replaced by new one. The deposition was carried out at room temperature (27°C) using unstirred solutions. By making several trials, deposition conditions were optimized.

The adsorption and reaction time was 50 Sec. Rinsing time was found to be 30 Sec. Thus single SILAR deposition cycle was made up of 50 Sec. adsorption of Cu^{2+} ions, 30 Sec. rinsing with double distilled water, 20 Sec. adsorption and reaction of S^{2-} ions and 30 Sec. rinsing with double distilled water. Figure 1 shows the flow chart of one SILAR deposition cycle of Cu_xS thin films formation.

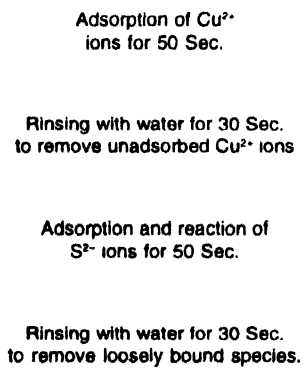

Figure 1. Flow chart showing one SILAR deposition cycle of Cu_xS thin film formation.

Film thickness of copper sulphide (Cu_xS) was determined by gravimetric weight difference method. For this, a sensitive microbalance was utilized and film density was assumed to be as bulk density of Cu_2S (5.6 gm/cm^3). By repeating such SILAR deposition cycles for 50 times, we have obtained good quality copper sulphide thin films of thickness of about 0.5 μm. Prolonging the deposition beyond 50 SILAR deposition cycles resulted in peeling of the films from the substrates.

2.2 Characterization of the films :

To study the effect of annealing, the films were annealed at temperature up to 500°C in an air for 1 h at the reported temperatures. The structural characterization of as deposited and annealed copper sulphide (Cu_xS) thin films were carried out by analyzing the X-ray diffraction (XRD) patterns obtained using a Philips PW-3710 X-ray diffractometer using *Cukα* radiations (λ = 1.5405 Å). Optical absorption studies were carried out using UV-VIS-NIR spectrophotometer (Hitachi, model 330, Japan) in the wavelength range 350-850 nm. The glass substrate was the reference for recording the absorption spectra.

3. Results and discussion

3.1 Structural properties :

It is reasonable to assume that the use of Cu(II) salt solution as a cationic precursor, would result in the formation of CuS thin films. However in our earlier studies, Cu_xS ($1.96 > x > 1.86$) and Cu_2S composition was observed. This could possibly result from the equilibrium

$$2Cu^{+} \Leftrightarrow Cu^{0} + Cu^{2+}$$

which would be displaced, perhaps through complexation depending on the nature of the complexing agent [18].

Figure 2 shows the XRD patterns of as deposited (CS_0) and annealed in air at 100 (CS_{100}), 200 (CS_{200}), 300 (CS_{300}), 400 (CS_{400}) and 500°C (CS_{500}), for 1 h. Cu_xS thin films on glass substrate. The broad hump is due to glass substrate. The standard *d* [19]

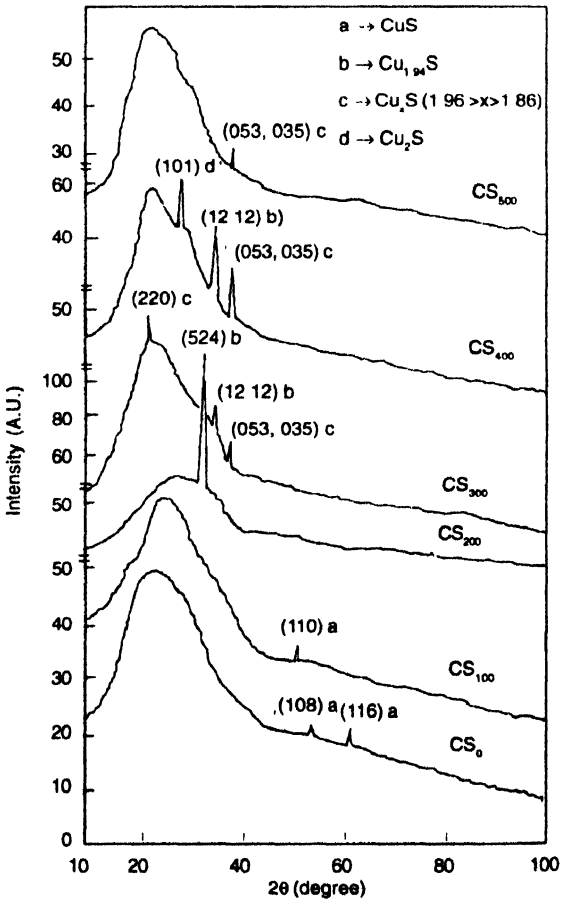

Figure 2. XRD patterns of Cu_xS films as deposited CS_0, annealed in air at 100°C (CS_{100}), 200°C (CS_{200}), 300°C (CS_{300}), 400°C (CS_{400}) and 500°C (CS_{500}) for 1h on glass substrates.

values of CUS, (ASTM 24-60), $Cu_{1.765}S$ (ASTM 23-960), $Cu_{1.8}S$ (ASTM 23-962), $Cu_{1.94}S$ (ASTM 23-956), Cu_xS ($1.96 < x < 1.86$) (ASTM 23-958) and Cu_2S (ASTM 24-57) were used for comparison with observed *d* values. Table 1 shows the comparison of standard and observed *d* values. It was observed that the as deposited film shows CuS (Covellite) composition. Annealing at 100°C does not make any change in composition. After annealing at 200°C, there was transition of CuS phase to $Cu_{1.94}S$ (djurleite), the peaks due to CuS were absent, whereas the major peak was due to $Cu_{1.94}S$. This indicates a complete transition of CuS phase to $Cu_{1.94}S$ phase. Annealing the film at 300, 400 and 500°C, there was further slight changes in the composition. All the as deposited and annealed films show hexagonal crystal structure. Air annealing at temperature 200°C leads to growth in grain size as illustrated by the improved sharpness of the XRD peaks. The intensities of the peaks were nearly constant for the samples annealed at 300-500°C.

Table 1. Comparison of observed and standard [19] *d* values for as deposited and annealed Cu_xS thin films.

Sample	Observed *d* values (Å)	Standard *d* values (Å)	Reflection plane (hkl)	Indentified phases
CS_0	1.71	1.73	108	CuS
	1.54	1.55	116	CuS
	1.21	1.21	213	CuS
CS_{100}	1.88	1.89	110	CuS
CS_{300}	3.04	3.04	524	$Cu_{1.94}S$
CS_{400}	3.90	3.88	220	Cu_xS (1.96<x<1.86)
CS_{400}	3.05	3.05	101	Cu_2S
	2.51	2.51	1212	$Cu_{1.94}S$
	2.31	2.30	053, 035	Cu_xS (1.96<x<1.86)
CS_{500}	2.32	2.30	053, 035	Cu_xS (1.96 <x<1.86)

The nearly 50% loss of sulphur from the films during annealing would take place through the loss of sulphur discarded at the film surface due to the decomposition : $2CuS \rightarrow Cu_{2-x}S + S\uparrow$. CuS is reported to decompose at ~ 220°C [20]. Melting of sulphur at 113-119°C and boiling at 445°C causes the decrease in crystallinity after annealing the samples above 200°C temperature.

3.2 *Optical properties :*

Figure 3 shows the plot of optical absorption coefficient (α) against wavelength (λ) for as deposited and annealed Cu_xS thin films at room temperature without accounting for reflection and transmission losses. The spectra showed clearly the absorption edge for as deposited films and the absorption edge shifted towards lower energy side for annealed samples. The data were analyzed from the following classical relation for annealed samples. The data were analyzed from the following classical relation for near optical absorption in semiconductor.

$$\alpha = \frac{K(h\nu - Eg)^{n/2}}{h\nu}$$

where K is a constant, Eg is the separation between the valance and conduction bands, n is a constant equal to one for direct

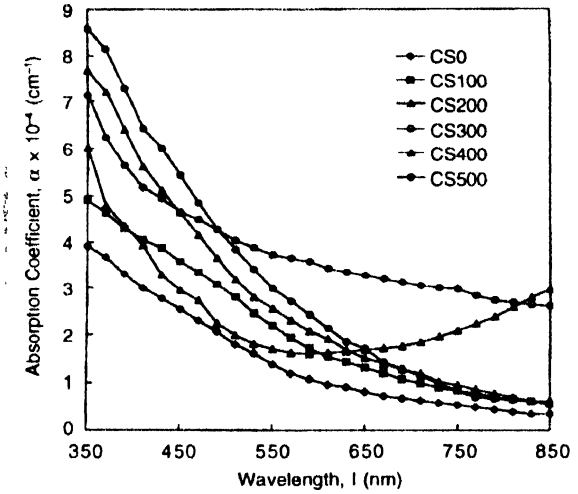

Figure 3. Variation of optical absorption coefficient (α) with wavelength (λ) of Cu_xS films as deposited CS0, annealed in air at 100°C (CS100), 200°C (CS200), 300°C (CS300), 400°C (CS400) and 500°C (CS500), for 1h on glass substrates.

gap materials and four for indirect gap materials. The variation of $(\alpha h\nu)^2$ *versus* $h\nu$ (Figure 4) is linear at the absorption edge confirms that as deposited and annealed copper sulphide $Cu_xS(1 \leq x \leq 2)$ is a semiconductor with a direct band gap. Extrapolating the straight line portion of the plot of $(\alpha h\nu)^2$ *versus* $h\nu$ for zero absorption coefficient value gives optical band gap

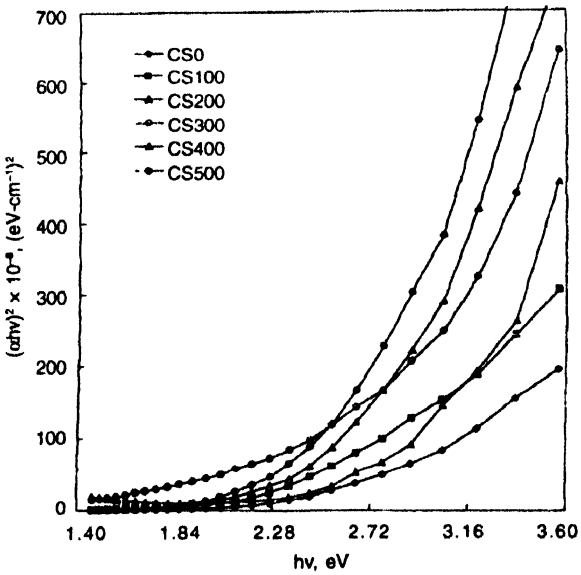

Figure 4. Plot of $(\alpha h\nu)^2$ *versus* $h\nu$ of Cu_xS films as deposited CS0, annealed in air at 100°C (CS 100), 200°C (CS 200), 300°C (CS300), 400°C (CS400) and 500°C (CS500), for 1h on glass substrates.

energy. Table 2 gives tabulation of band gap of as deposited and annealed copper sulphide (Cu_xS) thin films. Decrease in band gap energy with increase in annealing temperature may be attributed to the phase transition from one phase to another.

Table 2. Tabulation of optical band gap of as deposited and annealed copper sulphide (Cu_xS) thin films.

Sample	Optical band gap (eV)
CS_{0}	2.36
CS_{100}	2.32
CS_{200}	2.26
CS_{300}	2.16
CS_{400}	2.15
CS_{500}	2.11

4. Conclusions

In this paper, we have reported the deposition of copper sulphide (Cu_xS) thin films using simple successive ionic layer adsorption and reaction (SILAR) method. Use of triethanoloamine (TEA) as a complexing agent gives covellite CuS phase. By annealing the as deposited films at 200°C phase transition from 'copper deficient' (CuS) covellite phase to 'copper rich' djurleite phase is observed. Annealing at 200°C grain size increases significantly. Further, annealing above 200°C, decrease in crystallinity and phase transitions from djurleite to digenite and chalcocite phases is observed. Decrease in optical band gap energy with increase in annealing temperature may be attributed to transition from 'copper deficient' phase to 'copper rich' phase.

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References

[1] D C Reynolds, G Leies, L T Antes and R E Marburger *Phys. Rev.* 96 535 (1954)

[2] W Palz, J Besson, T N Dug and J Vedel *Solar Cells* (ed) C E Backus (New York : IEEE) p. 262 (1976)

[3] J J Loferski, J Shewchun, S D Mitlleman, E A Demeo, R Arnott H L Hwang, R Beauliew and G Chapman *Sol. Energy Mater* 1 157 (1979)

[4] K Okamoto and S Kawai *Jpn. J. Appl. Phys.* **12** 1130 (1973)

[5] S Couve, L Gouskov, L Szepessy, J Vedel and E Castel *Thin Solid Films* **15** 223 (1973)

[6] B Rezig, S Duchemin and F Guastavino *Sol Energy Mater* 2 53 (1979)

[7] H S Randhawa, R F Bunshah, D G Brock, B M Basol and O M Staffsudd *Sol. Energy Mater.* **6** 445 (1982)

[8] J A Thornton, D G Cornog, W W Anderson, R B Hall and J F Phillips *Proc. 16th IEEE Photovoltaic Specialists Conf* (San Diego) (New York : IEEE) p 737

[9] J F Jordan *Proc. 13th IEEE Photovoltaic Specialists Conf* (Scottsdale) (New York : IEEE) p 508 (1975)

[10] K W Boer and J D Meakin *Proc. Int. Workshop on Cadmium Solar cells and other Abrupt Heterojunctions* (University of delaware) (1975)

[11] *CdS Solar Cells Development NASA Rep* (R.-7296) Final Rep June (1971)

[12] R N Bhattacharya and P Pramanik *Bull. Mater. Sci* **3** 403 (1981)

[13] A J Varkey *Sol Energy Mater* **19** 415 (1989)

[14] M T S Nair and P K Nair *Semicond. Sci Technol* **4** 191 (1989)

[15] K M Gadave and C D Lokhande *Thin Solid Films* **229** 1 (1993)

[16] M T S Nair, L Guerrero and P K Nair *Semicond Sci. Technol* 13 1164 (1998)

[17] S D Sartale and C D Lokhande *Mater Chem. Phys* **65** 63 (2000)

[18] F A Cotton and G Wilkinson *Advanced Inorganic Chemistry* p 801 (New York · Wiley Interscience) (1980)

[19] ASTM X-ray Data File Nos 24-60, 23-960, 23-962, 23-956 23-958, 24-57

[20] G H Aylward and T J V Findlay *SI Chemical Data* p34 (Melbourne Australia : John Wiley) (1974)